

Polycyclic Aromatics, Fullerenes and Soot Particles as Charged Species in Flames

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1. INTRODUCTION AND EXPERIMENTAL

The ionic structure of fuel-rich hydrocarbon flames resembles the profiles of the larger neutral intermediates much more than those of initial reactants and main products. This applies in particular to polycyclic aromatic hydrocarbons (PAH). They have low and rather similar ionization potentials and relatively large proton affinities. The pattern of reactions of positive ions, condensation and cyclization reactions, shows many similarities with the behavior of their neutral counterparts. Apart from the predominance of some PAH⁺ with an odd number of C atoms, which would be radicals in the neutral state, the occurrence of PAH⁺ is an indication of the existence of the respective neutral compounds. Thus, large flame ions, their composition, reactions and equilibria at high temperature are not only of interest for themselves, but also reflect the existence and behavior of large neutral PAH. The discussion of fullerenes in flames has still to be based solely on their ions.

The experimental procedure of sampling 26.6-mbar flat premixed flames via a two-stage nozzle/molecular beam sampling system and analyzing the ions by a time-of-flight MS has been reported [1, 2]. Recently, the MS was modified by adding a Mamyrin-type ion reflector, thereby increasing the mass resolution $(m/\Delta m)_{\text{ex}}$ to about 1500. The flight time was determined by a multi-stop time-to-digital converter. Ion signals from about 20.000 extraction pulses were summed up to give the mass spectrum. Details will be published elsewhere [3].

2. POLYCYCLIC AROMATIC HYDROCARBON IONS (PAH⁺)

The main formation of the PAH⁺ in sooting flames takes place in the oxidation zone where their concentrations go through maxima (Fig. 1) [2]. The decrease of the PAH⁺ with $m < 325$ u after their maxima is due to thermal decomposition, probably initiated by oxidative attack. It takes place almost simultaneously for these lower-mass PAH⁺. The larger PAH⁺ with $m \geq 325$ u continue to grow as shown by the shift of their maxima to greater heights with increasing mass. The largest PAH⁺ in acetylene flames reach masses of about $2.5 \cdot 10^3$ u.

PAH⁺ occur with any number of C atoms and those with a certain carbon content contain a varying number of hydrogen atoms (Fig. 2). The number of H atoms points to certain structures. Other arguments in this respect are the thermal stability, the relation to identified neutral PAH and the occurrence of certain side chains, the prevalence of peri-condensation and the possibility of protonation and deprotonation as a function of temperature.

The relatively large concentration of $C_{13}H_9^+$ in C_2H_2 flames, an indication of little reactivity, is a strong argument for the stable fully condensed phenalenylium (I):



(I)



(II)

Other isomers such as (II) would be less stable. The far less thermally stable dihydro-compound, $C_{13}H_{11}^+$, occurs in extremely low concentration. At higher temperature, $C_{13}H_7^+$ is formed, an ion that cannot be formulated as a tricyclus without assuming a benzyne bond which was never observed in flame components. A more probable structure, compatible with structural elements normally found in PAH, would be:



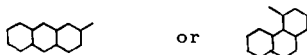
It could be formed by thermal decomposition from phenalenylium via retro-insertion out of a six-membered ring followed by H_2 elimination from the resulting side chain. Structures with side chains

containing triple bonds are suggested for the relatively hydrogen-poor PAH⁺ with $m \lesssim 300$ u. It is known from butadiyne pyrolysis that such side chains are split off from PAH at temperatures $\gtrsim 1400$ K [4]. This would fit the finding that the lower-mass PAH⁺ decompose thermally in a flame zone where polyynes are formed.

A $C_{13}H_{7.2}^+$, being present in appreciable concentration compared to a main PAH⁺ $C_{13}H_7^+$, indicates a change in the carbon skeleton rather than hydrogenation. For $C_{13}H_9^+$ probable structures are

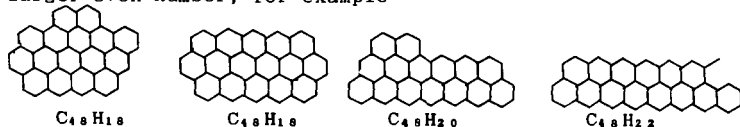


while $C_{13}H_{11}^+$ is rather a tricyclus with a CH_2 group

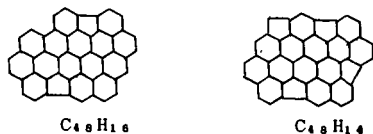


Protonation enlarges the variation in the number of H atoms of even-numbered PAH⁺ without change in the carbon skeleton (Fig. 2). Another example is the C_{16} -PAH which is present as $C_{16}H_{11}^+$ (protonated pyrene or less probable fluoranthene, closed-shell ions) and $C_{16}H_{10}^+$ (ionized pyrene, radical ion). At lower temperature the protonated PAH is formed, but at higher temperature the latter attains even larger concentrations. $C_{16}H_9^+$ which is assumed to be a butadiynyl-acenaphthylene ion is also formed at high temperature.

For larger PAH, the number of H atoms depends on the arrangement of rings. Divergence from a more circular system to an elongated or ribbon-like PAH increases the number of hydrogen atoms by 2 or a larger even number, for example



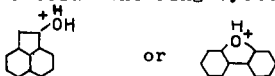
On the other hand



Formation of 5-rings condensed with the 6-rings diminishes the number of H atoms by 2 or a multiple thereof. This possibility of forming relatively hydrogen-poor PAH⁺ is held more probable for high-mass ions.

Of the many possible variations in the number of H atoms for a fixed number of C atoms only a few, seldom more than 3 for odd-numbered and 4 for even-numbered PAH⁺, are realized, even in the case of large PAH⁺. Although there are shifts in the abundance of H-rich and H-poor PAH⁺ with temperature, there is always one certain C-H-composition that dominates in a group of ions with the same number of C atoms. This is always compatible with a highly condensed arrangement of 6-rings with one or no 5-ring. However, in the case of large PAH⁺ these predominant C-H-compositions would also fit to elongated or ribbon-like ring arrangements with an increased number of 5-rings. This option would be in favor of fullerene formation, see below.

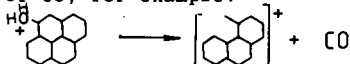
Oxo-PAH⁺, such as C₁₂H₈O⁺, C₁₆H₁₀O⁺ and C₁₈H₁₂O⁺ up to C₂₄H₁₆O⁺, are intermediates in fuel rich benzene flames. They occur together with PAH⁺ [5]. Probably, the positive charge is located on an O atom outside the ring system, for example:



This structure is more stable than

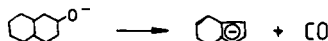


Oxo-PAH⁺ are thermally less stable than PAH⁺ with the same number of C atoms. A primary decomposition step of oxo-PAH⁺ probably is the elimination of CO, for example:



This mechanism of PAH⁺ formation is not taking place in acetylene flames, since no oxo-PAH⁺ are formed from this fuel. Many PAH⁺ in benzene flames contain two more H atoms and probably have structures different from those with the same number of C atoms in acetylene flames. C₁₂H₈⁺ is missing in benzene flames since there is no easy mechanism by which it could be formed through CO elimination from C₁₄H₈O⁺. High-resolution mass spectrometry will show whether such differences in H content do also occur in larger PAH⁺. This might have to do with the stop of PAH⁺ growth at 900 to 1000 u and the absence of charged soot particles in benzene flames up to a C/O = 0.93.

Oxo-PAH⁻ which are only formed in flames of aromatic fuel also decompose within the oxidation zone by elimination of CO giving PAH⁻, for example:



The resulting PAH⁻ with their comparatively stable cyclopentadienyl anion structure, also unique in benzene flames, do not show further growth. That the negative charge of oxo-PAH⁻ is located on the O atom is supported by the fact, that they are able to grow by condensation reactions with lower unsaturated hydrocarbons.

3. POSITIVELY CHARGED SOOT PARTICLES

PAH⁺ with $m \geq 350$ u grow continuously until their average mass reaches about 800 to 1400 u in sooting acetylene flames. Then a new broad distribution of masses ranging from about 2.5 to $7 \cdot 10^3$ u appears. It has a flat maximum at about $4 \cdot 10^3$ u (Fig. 3, 11mm). This is due to the first charged soot particles. About 0.3 ms later (12 mm), it has increased in intensity, peaks at $5 \cdot 10^3$ u and extends to 10^4 u. Meanwhile, the large PAH⁺ have disappeared to a large degree. Instead of a continuous shift of the PAH⁺ distribution into the range of the beginning charged soot, there remains a minimum at about $2 \cdot 10^3$ u. This behaviour is interpreted as a switch from a mainly two-dimensional growth of the PAH⁺ to a three-dimensional growth of soot particles, initiated by sticky collisions of large PAH⁺ with neutral PAH of the same mass range. The total ion concentration stays almost constant between 11 and 12 mm [1].

From 14 mm on, the number density of charged soot particles increases strongly because of the onset of thermal ionization. The further development of the particle mass distributions is shown on Fig. 4, obtained from measurements using a combination Wien-filter/energy discriminator for mass analysis [6].

At the start of soot formation in acetylene flames, the fraction of positively charged soot is very low, of the order of 1 %. It increases to 30 - 40 % (depending on the burning conditions) when the single particles have reached their final size [7]. Thus, the largest part of positively charged soot is formed by thermal ionization from neutral soot and not as a consequence of growth of PAH⁺. Most of the charged particles carry a single charge. With increasing flame temperature the fraction of doubly charged particles increases up to about 10 %. There is also negatively charged soot. It is formed somewhat later and its amount does not reach that of the positively charged soot (15 to 25 %). The percentage decreases with increasing flame temperature. As pointed out, PAH⁻ do not grow. Therefore, there is no connection between PAH⁻ and the first negatively charged soot which most probably is formed by electron attachment to neutral particles.

In benzene flames (for C/O < 0.93) the growth of PAH⁺ stops at about $1 \cdot 10^3$ u and only neutral soot is formed thereafter. The reason for this behavior of PAH⁺ is not quite clear. The lower concentration of acetylene and polyynes, the higher temperature together with the partly different structure of PAH⁺ in benzene flames might be the reason. The lack of thermal ionization of soot is caused by the smallness and the slow growth of the first particles in low-pressure benzene flames which is also correlated with the lower concentration of highly unsaturated aliphatics.

4. FULLERENE IONS

Fullerene ions of both sign cover a much larger mass range than PAH ions. The smallest positive ion detected in benzene flames is C₂₂⁺ (384 u). The largest one in sooting acetylene flames exceeds C₅₀₀⁺ (6000 u) as shown by the mass spectrum in Fig. 5. Generally, there are a few outstanding peaks (C₅₀, C₆₀, C₇₀, C₇₄, C₈₂, C₈₄) and a much larger number of quasi-continuously distributed species [5]. A mass spectrum of negative fullerene ions from

the burned gas of a benzene flame in Fig. 6 shows the same general appearance. It differs, however, in some details such as the formation of very small fullerenes like C_{34}^- (smallest in acetylene flames is C_{44}^-) and the occurrence of odd-numbered fullerenes containing 1 to 2 H atoms centered around C_{50}^- and (to a less degree) around C_{70}^- . There are further differences in the ion abundances depending on the height in the flame, the sign and the burning conditions.

The largest difference in the nature of fullerene ions is caused by the onset of soot formation. Fig. 7a demonstrates the change in the fullerene mass spectrum from the soot-free oxidation zone to the soot-forming zone in the burned gas of the same benzene flame. A principally similar result was obtained with mass spectra from the burned gas of acetylene flames below and above the critical C/O for soot formation, see Fig. 7b. In both cases the overall abundance of the ions increases and the quasi-continuous distribution of the heavier fullerenes appears when soot is formed. There are mainly some of the outstanding peaks where the fuel-rich flames are free of soot.

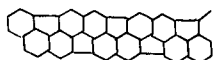
In acetylene flames, where the oxidation and the soot-forming zone is clearly separated, the concentration of fullerenes drops to very low values where the temperature is near its maximum and the O_2 is not yet completely consumed. This minimum is specially marked for negative fullerene ions. It is interpreted as burning of the lower-mass fullerenes. A decrease in the total negative ion concentration may contribute to this effect [1]. In benzene flames where these two zones overlap the intermediary decrease is weak for negative fullerenes and not expressed in the positive ion profiles. Formation of fullerenes in the oxidation zone can be suppressed by increasing the temperature.

In the secondary reaction zone of the flame, where O_2 is not yet completely consumed, large fullerene ions of vastly different mass are formed almost simultaneously in the presence of soot. The profiles do not indicate a growth of fullerenes. They reach a second maximum in the burned gas and also decrease simultaneously, probably by charge recombination. The formation of the "prominent" fullerene ions (C_{50} , C_{60} , C_{70}) in this zone is more or less retarded, depending on the burning conditions. In particular, C_{60}^- increases steadily in the burned gas where large negative fullerenes decrease.

While the formation of large PAH may in principle be explained by the growth of lower mass species through reaction with unsaturated C_2^- , C_3^- and C_4^- hydrocarbons and/or the respective radicals, this is not so for the fullerenes. C_{60}^+ is always the first to be observed without being preceded by lower-mass fullerenes. It lies between the C_{54}^- and C_{56}^- PAH⁺ in the mass spectrum. But these species contain between 18 and 20 H atoms and therefore have quite a different structure. The question is, how might closed-cage molecules (or ions) with 12 five-membered rings be formed in a homogeneous reaction without going through intermediates with too much ring tension.

If the mass spectrum of PAH⁺ is searched for possible "pieces" of C_{60}^+ , the free valencies of which being saturated by H, there are mainly smaller mass PAH⁺ up to 250 u, the C skeletons of which are structural elements of C_{60} . Mass 250 ($C_{20}H_{10}$) could represent a PAH consisting of five 6-rings surrounding one 5-ring. $C_{30}H_{12,13}$ with mass 372 and 373 u which would be the molecular formula for one

"half" of a C_{60} occurs only in very minor concentration. A formation of C_{60} by reactive collision of two half-shells would be too slow because of the low concentrations of the reactants. There is an ion with composition $C_{30}H_6^+$ in very low abundance, which does not fit any C_{60}^+ fragment. The fact that large PAH⁺ with very low hydrogen content could not be detected, indicates that the loss of hydrogen and the formation of most of the 5-rings takes place simultaneously in late stages before completion of the ball. A possible mechanism along these lines might be the following: If two 6-rings at the poles of C_{60} are removed, there remains a closed ribbon of 48 C atoms that unwrapped has the structure



This would correspond to $C_{48}H_{12}$ which is the main C_{48} -PAH⁺. It contains the structural elements of acenaphthylene and benzo[ghi]perylene which are quite common among the PAH. As the number of 5-membered rings is relatively low for the size of the ring system and they are condensed only with four 6-rings, there is no serious ring tension. The molecule bends almost by itself towards closing of the ribbon, see Fig. 8. Most of the C_{48} -PAH⁺ will have flat structures given in section 2, but a few percent might be ribbon-shaped. Addition of two benzene molecules and a rapid stepwise formation of C-C bonds by an intramolecular condensation with simultaneous splitting off of H_2 , while double bonds are regenerated, could finally give C_{60} . This accumulates because of its chemical inertness. The fact that fullerene concentration may be up to ten times larger in benzene flames than in acetylene flames might be an indication that reactions with benzene are important steps. A similar mechanism could be possible for C_{70} . However, there is still no indication how the large fullerenes could be formed, other than probably by heterogeneous reaction which involves very small soot particles.

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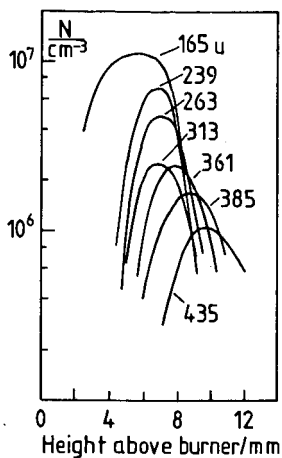


Fig. 1 PAH⁺ profiles in a sooting C_2H_2/O_2 flame; $C/O = 1.12$; $p = 26.6$ mbar
 $v_u = 42$ cm/s

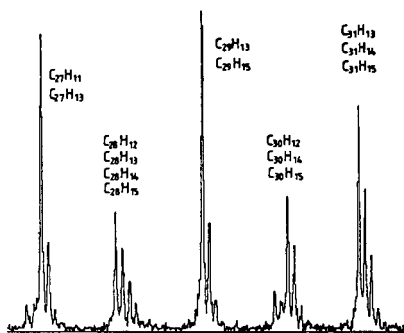


Fig. 2 PAH⁺ with the same number of C occur with different numbers of H; $C_2H_2/O_2 = 1.0$; $p = 26.6$ mbar
 $v_u = 42$ cm/s; $h = 12$ mm

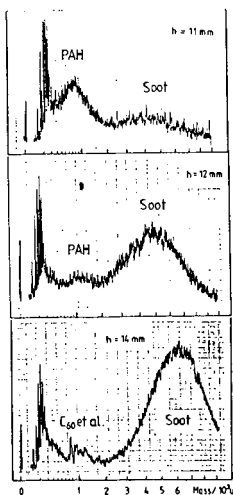


Fig. 3 Mass distributions at the transition from PAH⁺ to charged soot particles; $C_2H_2/O_2 = 1.12$
 $p = 26.6$ mbar; $v_u = 42$ cm/s

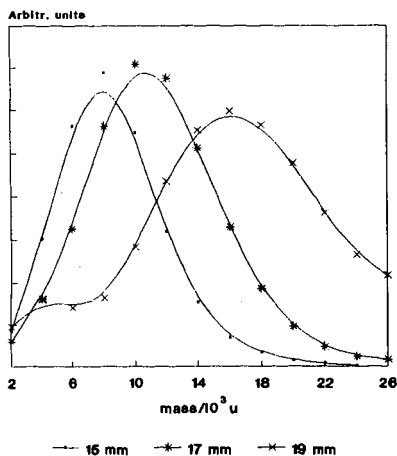


Fig. 4 Mass distribution of charged soot particles in a C_2H_2/O_2 flame; $C/O = 1.06$; $p = 26.6$ mbar;
 $v_u = 50$ cm/s

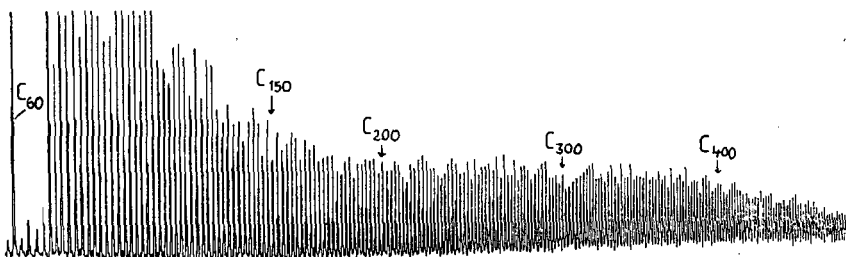


Fig. 5 Mass spectrum of positive fullerene ions from a sooting C_2H_2/O_2 flame; C/O = 1.0, h = 20 mm, p = 26.6 mbar, $v_u = 42$ cm/s. The peaks to C_{104} are truncated.

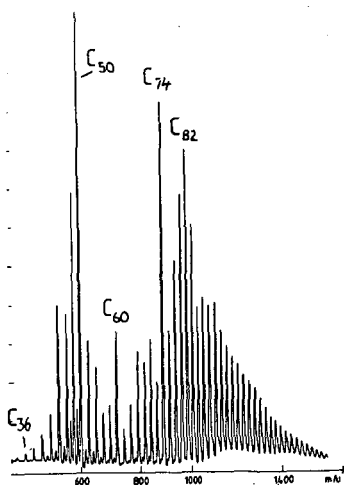


Fig. 6 Mass spectrum of negative fullerene ions from a benzene/oxygen flame; C/O = 0.76, $h = 12$ mm, $p = 26.6$ mbar, $v_u = 42$ cm/s

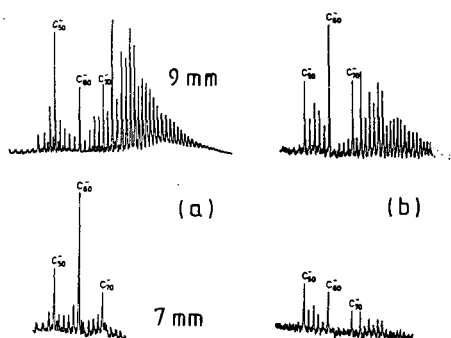


Fig. 7a Negative fullerene ions in the soot-free oxidation zone (7 mm) and in the sooting zone (9 mm) of a $C_{6}H_6/O_2$ flame; $C/O = 0.76$, $v_u = 42$ cm/s; 7b: The same ions in the burned gas of a non-sooting (below, $C/O \approx 0.84$) and a sooting ($C/O = 0.90$) acetylene/ O_2 flame; $h = 28$ mm, $v_u = 42$ cm/s

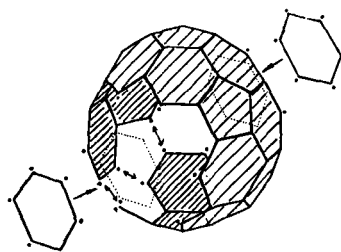


Fig. 8 Tentative mechanism of C_{60} formation from a bent ribbon-shaped PAH $C_{48}H_{18}$ and two benzene molecules. The dots mark C atoms which carry H atoms while the hidden ones are not marked.